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AFRPL-TR-68-144

(TITLE UNCLASSIFIED)

**INVESTIGATION OF THE THERMODYNAMIC
PROPERTIES OF PROPELLANT INGREDIENTS**

QUARTERLY PROGRESS REPORT AFRPL-TR-68-144

(1 April 1968 to 30 June 1968)

July 1968

**AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
EDWARDS AIR FORCE BASE, CALIFORNIA**

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**(Prepared under Contract Nr. F04611-67-C-0025 by
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QUARTERLY PROGRESS REPORT (U)
(1 April 1968 to 30 June 1968)

July 1968

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CHEMICALS LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN 48640

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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract Nr. FO4611-67-C-0025. The contract was initiated under Air Force Program Nr. 750 G, AFSC Project Nr. 3148, "Investigation of the Thermodynamic Properties of Propellant Ingredients." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. Curtis C. Selph acting as Air Force Project Officer.

This is the second quarterly report, covering the work performed during 1 April 1968 through 30 June 1968. The Dow Report Number is T0025-2Q-68.

This work was performed under the technical supervision of Dr. D. R. Stull and management supervision of Dr. D. A. Rausch, with Dr. G. C. Sinke as Group Leader.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

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ABSTRACT

(C) Heat of combustion measurements on perfluoroammonium fluoroborate from Shell Development Company gave erratic results. The amount of sample available is limited and not sufficient to allow tracing down the reasons for the failure of this technique. A differential scanning calorimeter requiring only a few milligrams of sample was successfully used to measure the heat of decomposition and this approach yielded a preliminary heat of formation of -319 ± 10 kcal/mole. Further work on the heat of decomposition is planned to improve the accuracy and to better establish the products of decomposition.

(C) The heat of formation of a sample of aminoethylaziridine (Code ELF-100), $C_4H_{10}N_2$, from Esso Research and Engineering Company was derived as +12.68 kcal/mole from heat of combustion measurements. Work on methyldiazabicyclo-octane (Code ELF-101), $C_7H_{14}N_2$, also from Esso, revealed the heat of combustion to be decreasing with time, indicating some slow chemical change taking place. No accurate heat of formation could be obtained.

(U) The heat of combustion of aniline hydrochloride (synthesized at Dow) was measured and a new computerized data reduction program used to derive a heat of formation of -43.0 kcal/mole. This is in reasonable agreement with -42.0 kcal/mole from heat of solution data and it is concluded that no serious systematic errors remain in the data reduction program.

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THERMOCHEMISTRY OF PROPELLANT INGREDIENTS (U)

A. HEAT OF FORMATION OF PERFLUOROAMMONIUM FLUOBORATE (C)

1. Introduction (U)

(C) Perfluoroammonium fluoborate (NF_4BF_4) has been synthesized at Shell Development Company. A 5 gram sample was supplied to us for thermochemical studies. As outlined in our first quarter report for 1968, we proposed to measure the heat of combustion of NF_4BF_4 by the technique of Good and Mansson (1). As will be described in the following sections, this approach proved unsuccessful. A preliminary value for the heat of formation was obtained, however, by differential scanning calorimetry.

2. Materials (U)

(C) Polypropylene film and polyvinylidene fluoride (Kynar) were described in the first quarter report. The Kynar sample was checked for water content before and after drying at 120°C . for 16 hours and the results indicated no loosely bound water which might react with the NF_4BF_4 .

(C) The NF_4BF_4 was a white free flowing crystalline material. Analytical data supplied by Shell Development Company showed the sample to be of high purity. Due to the limited amount of sample, no confirmatory analytical experiments were carried out at Dow. The sample is reported to be highly reactive to moisture and was stored in a monitored dry box.

3. Equipment (U)

(U) A typical rotating bomb calorimeter and a platinum lined combustion bomb were employed for heat of combustion studies. A Perkin-Elmer Differential Scanning Calorimeter (hereafter referred to as DSC) was used for heat of decomposition work.

4. Heat of Combustion Procedure (U)

(C) A weighed polypropylene bag containing a weighed amount of Kynar was locked into a dry box. Approximately the desired amount of NF_4BF_4 was weighed out on a small balance in the dry box and added to the polypropylene bag. The bag was heat sealed while in the dry box and the Kynar and NF_4BF_4 intimately mixed by manipulation of the sealed bag. A pinhole was pricked in the bag to allow trapped gas to escape and the bag was rolled up and compressed in a press to form a pellet. The pellet was placed in a second weighed polypropylene bag which was then heat sealed, removed from the dry atmosphere, and accurately weighed. The sample thus enclosed did not pick up weight when weighed in the laboratory air.

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(U) The weighed sample was placed in a platinum crucible in a platinum-lined bomb. The bomb also contained 10 ml of water and after sealing was charged with purified oxygen to 40 atm pressure. The heat of combustion was determined by the usual techniques. A sample of the gaseous combustion products was analyzed by mass spectrometry.

5. Heat of Combustion Results (U)

(C) A brief summary of the heat of combustion results is given in Table I. The experiments by visual observation of the bomb after combustion appeared to be successful in that no unburned residues were observed and mass spectrometry revealed the expected gaseous products CO_2 and traces of CF_4 . The calculated heats of combustion, however, showed wide variations. Possible causes for these variations were researched as follows:

- (a) Deterioration of the Sample - A few milligrams of sample were allowed to stand exposed to the dry box atmosphere over the weekend. No changes in the sample appearance were observed, making deterioration an unlikely cause.
- (b) Water Associated with the Kynar - Karl Fischer analyses for water before and after drying the Kynar at 120°C overnight indicated no appreciable water in the Kynar.
- (c) Incomplete Combustion - Visual inspection of the bomb and mass spectrometer analysis of gaseous products showed no evidence for incomplete reaction.
- (d) Reaction of Kynar and NF_4BF_4 - This appears to be the only plausible cause, but if it took place to the extent indicated by the heat of combustion data one would expect considerable and obvious gas formation in the sealed bags. This was not observed.

Because of the limited amount of sample and the considerable expense of its synthesis, it was not practical to investigate variations in the heat of combustion technique. Chances of success were believed too small to risk the use of more sample.

6. Differential Scanning Calorimeter Technique (U)

(U) The Thermal Research Laboratory recently acquired a Perkin-Elmer Differential Scanning Calorimeter which is suited for measurement of heat capacity, heats and temperatures of phase transitions, and heat of reaction with moderate accuracy. The advantage of the DSC is that results can be obtained on a few milligrams of sample. The sample is enclosed in a small aluminum capsule and is then heated so that its temperature rises at the same rate as that of a reference capsule containing the calorimetric standard material, Al_2O_3 . The rate at which energy is supplied to the sample is

recorded and, for example, if a sample undergoes melting, a peak is observed in the rate of heating, since the heat of melting must be supplied in a short time. From the area under the peak, the heat of melting can be determined.

Table I

Heat of Combustion of NF_4BF_4 (C)

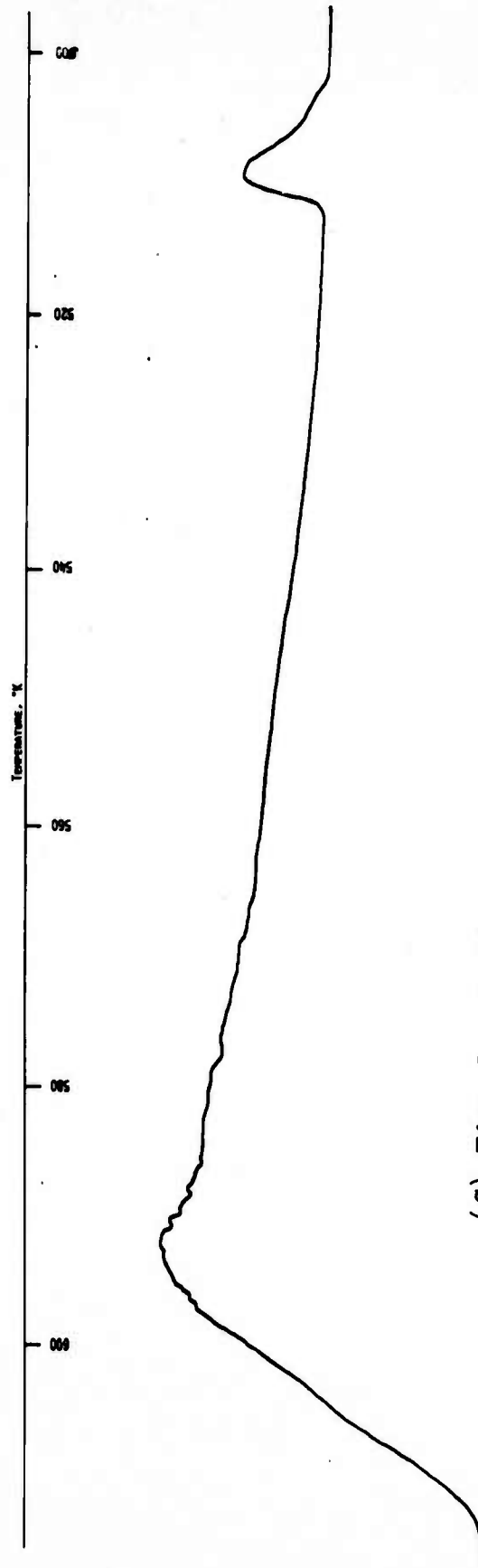
<u>Expt. No.</u>	<u>Mass Poly- propylene, grams</u>	<u>Mass Kynar, grams</u>	<u>Mass NF_4BF_4, grams</u>	<u>$-\Delta E_c/M$, cal/g</u>
1	0.13076	1.38462	0.06738	1003
2	0.13983	1.67173	0.68265	990
3	0.10523	1.36214	0.49074	522
4	0.15707	1.32800	0.48851	743

(C) Since Shell Development Company personnel reported to us that NF_4BF_4 decomposes to NF_3 , BF_3 , and F_2 at relatively low temperatures, it seemed worthwhile to attempt a measurement of the heat of decomposition in the DSC. Preliminary measurements at Shell indicated a heat of decomposition of about 8 cal/gram.

7. Differential Scanning Calorimeter Results (U)

(U) A copy of the recorder output (heating rate) as a function of temperature is shown in Figure 1. The sample when heated showed a small increase in heat absorption in the range 500-510°K. Heating was stopped at about 520°K and the capsule containing the sample was cooled and weighed. Only 2 to 3% of the sample weight was lost, and it was concluded that the heat absorption was a reversible phase transition. This was confirmed when the sample was heated again to 520°K and the same heat absorption was observed at 500-510°K. Integration of the area under the peak gave a heat of transition of 13 cal/g. It seems likely that it was this heat of transition which was observed by Shell Development Company personnel.

(C) Heating was now continued above 520°K and at about 560°K it was evident that an endothermic process was taking place. Also the instrument exhaust port began fuming, evidencing the effluence of reactive vapors. This endothermic process appeared to be completed by 620°K, at which point the capsule was cooled and weighed. A weight loss corresponding to 99.5% of the sample was observed. From the area under the peak it was roughly calculated that the heat of decomposition was 80 cal/g. This is somewhat uncertain because of difficulty in judging where to draw the baseline. The corrosive vapors emitted by the sample had seriously affected the



(C) Fig. 1 - Differential Scanning Calorimeter Trace of Decomposition of NF_4BF_4

instrument as shown by blank runs following this work. For this reason no further runs were made and the single heat of decomposition obtained is probably uncertain by 40 cal/g. If the decomposition is, as claimed by Shell Development Company, to NF_3 , BF_3 , and F_2 , the above heat of transition and heat of decomposition give:

$$\Delta H_{298}^{\circ}(\text{NF}_4\text{BF}_4, \text{s}) = -318.8 \pm 10 \text{ kcal/mole}$$

(NF_3 is taken as -31.6, BF_3 as -217.7 kcal/mole). It may be observed here that this heat of decomposition implies that the heat of combustion should be 1100 cal/g, considerably higher than any of the experimental results.

8. Work in Progress on NF_4BF_4 (C)

(C) Because of corrosion of the DSC, as well as inability to examine decomposition products, we propose to measure the heat of decomposition by a modified bomb calorimeter approach. A nickel crucible was wound with a glass insulated constantan heater and suspended in a nickel combustion bomb. When the sealed bomb was placed in a combustion calorimeter and the crucible electrically heated, the crucible became hot enough to decompose NF_4BF_4 and the electrical heat was about equal to that of a typical combustion experiment. Blank runs showed excellent precision. However, when a sample of NF_4BF_4 was tried, an exotherm was observed rather than the expected endothermic effect. Mass spectrometer examination of the gases showed the expected NF_3 , but also large amounts of SiF_4 rather than BF_3 . The reaction of the F_2 and BF_3 with the very dry glass insulation was not expected, since there are literature reports of successful fluorine combustion work carried out in glass apparatus.

(U) Work is now in progress on a new double-walled crucible with the aim of protecting the heater winding from the corrosive vapors. Should this prove successful, we should be able to obtain a heat of decomposition with high accuracy and also to analyze the products of decomposition to make sure that the mechanism of decomposition is as postulated for the DSC experiments.

B. HEATS OF COMBUSTION OF AMINOETHYLAZIRIDINE AND METHYLDIAZABICYCLO-OCTANE (C)

1. Introduction (U)

(C) Esso Research and Engineering Company has synthesized several C-H-N compounds as candidate fuels. Work on the heat of combustion of two of these compounds is reported here: aminoethylaziridine, $\text{C}_4\text{H}_{10}\text{N}_2$ (Code ELF-100), and methyldiazabicyclo-octane, $\text{C}_7\text{H}_{14}\text{N}_2$ (Code ELF-101).

2. Materials (U)

(U) Correspondence from Esso Research and Engineering Company stated the materials were "analytically pure as attested to by C-H-N analysis, NMR, and IR." The samples were liquids of low vapor pressure but appreciable reactivity with respect to absorption of water and CO₂. Two different batches of ELF-100 were received and one batch of ELF-101.

(U) A check on these samples was made by neutron activation analysis for oxygen. Our results showed 0.56 weight % oxygen in the ELF-100 and 0.25 weight % oxygen in ELF-101. Further work is in progress to check these data by other methods and to define the nature of the oxygen-containing impurity.

3. Equipment (U)

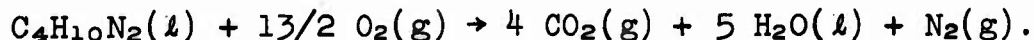
(U) A typical rotating bomb calorimeter and a platinum lined combustion bomb were employed.

4. Procedure (U)

(U) Tests showed that samples enclosed in Mylar film picked up weight when exposed to the atmosphere, presumably by diffusion of moisture through the plastic. Samples were therefore loaded in a dry atmosphere into thin walled glass ampoules which were sealed off. The weighed ampoules were placed in a platinum crucible and a small weighed amount of paraffin oil was added. The bomb was charged in the usual way and fired electrically. The paraffin oil ignited and the heat burst the sample ampoule, allowing its contents to burn completely. After the calorimetry the bomb was rinsed out and the solution titrated for HNO₃ formation.

5. Results (U)

(C) Results were calculated by computer using standard procedures. Constant factors employed in the calculations are given in Table II and data for the individual experiments in Tables III, IV, and V. The average result for ELF-100 from Table IV and a molecular weight of 86.1377 yields $\Delta E_{c298}^{\circ} = -729.57 \pm 0.51$ kcal/mole for the constant volume process:



Calculating to constant pressure conditions gives:

$$\Delta E_{c298}^{\circ} = -730.46 \pm 0.51 \text{ kcal/mole}$$

from which is derived:

$$\Delta H_{f298}^{\circ}(l) = +12.68 \pm 0.51 \text{ kcal/mole.}$$

The error is twice the standard deviation of the experiments and does not include any corrections for impurities.

Table II

(C) Constant Factors for Heat of Combustion Calculations

Empirical formula, ELF-100	$C_4H_{10}N_2$
Empirical formula, ELF-101	$C_7H_{14}N_2$
Empirical formula, paraffin oil	$CH_{1.8374}$
Empirical formula, Mylar film	$C_{10}H_8O_4$
Empirical formula, fuse	$CH_{1.800.8}$
Density of ELF-100, g/cc	0.986
Density of ELF-101, g/cc	0.899
Density of paraffin oil, g/cc	0.89
Density of film, g/cc	1.38
Density of fuse, g/cc	1.5
Bomb volume, liter	0.347
Initial oxygen pressure, atm	30.3
Initial water, liter	0.001*
Reference temperature, °C	25.00
$(\partial E/\partial P)_t$ of ELF-100 and ELF-101, cal/g/atm	-0.00189
$(\partial E/\partial P)_t$ of paraffin oil, cal/g/atm	-0.00614
$(\partial E/\partial P)_t$ of film, cal/g/atm	-0.00080
ΔE_c° of film, kcal/mol	-104.89
ΔE_c° of fuse, kcal/mol	-111.7
C_p of ELF-100 and ELF-101, cal/g/°C	0.5
C_p of oil, cal/g/°C	0.5
C_p of film, cal/g/°C	0.315
C_p of fuse, cal/g/°C	0.4
E (calor) for ELF compounds, cal/°C	3414.71
E (calor) for paraffin oil, cal/°C	3427.20

*Exp. 9B - 0.002 liter.

Exp. 10 - 0.010 liter.

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Table III

(U) Heat of Combustion Experiments for Paraffin Oil

	Experiment No.				
	1	2	3	4	5
Paraffin oil, g	0.617860	0.629315	0.635555	0.623490	0.620375
Fuse, g	0.003105	0.001762	0.002325	0.002290	0.002050
t_i , °C	22.966760	22.966750	22.966740	22.966700	22.966670
t_f , °C	25.024040	25.057450	25.077540	25.039940	25.029350
Δt_{corr} , °C	0.072730	0.070930	0.069900	0.071090	0.071430
$-\Delta E_c/M$, cal/g*	-10987.70	-10988.06	-10990.57	-10990.45	-10986.89
	6	7	8	9	10
Paraffin oil, g	0.573732	0.575125	0.570325	0.573465	0.556385
Polyester film, g	0.101800	0.098865	0.100370	0.090380	0.099555
Fuse, g	0.003715	0.002800	0.003395	0.003315	0.002985
t_i , °C	22.966720	22.966740	22.966720	22.966710	23.004490
t_f , °C	25.045280	25.041740	25.031040	25.024170	25.024730
Δt_{corr} , °C	0.072110	0.070510	0.072070	0.070910	0.07406
$-\Delta E_c/M$, cal/g*	-10991.19	-10986.86	-10987.20	-10988.66	-10989.65

* $\Delta E_c/M$ (average) = 10988.7 cal/g.

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Table IV

Heat of Combustion Experiments for ELF-100

Parameter	Experiment Number					
	1	2	3	4	5	6
ELF-100, g	0.65972	0.63410	0.42972	0.59791	0.428383	0.57337
Paraffin oil, g	0.11292	0.19047	0.31966	0.19847	0.40557	0.30010
Fuse, g	0.00271	0.002720	0.00285	0.002196	0.003364	0.002352
Mole of $\text{HNO}_3 (\times 10^3)$ final	1.197	1.164	0.899	1.090	0.888	1.100
Mass of glass, g	0.1321	0.1593	0.1133	0.1272	0.0683	0.1349
Mass of added Pt., g	51.0461	51.0461	51.0279	51.0279	51.0279	51.0279
t_i , °C	22.91021	22.71656	22.86632	22.84750	22.56786	22.58572
t_f , °C	24.98126	24.97797	25.02991	25.03803	25.00303	25.03548
Δt_{corr} , °C	0.06481	0.06884	0.06210	0.06231	0.05966	0.06182
$-\Delta E_c/M$, cal/g	-8,463.50	-8,469.52	-8,473.32	-8,469.14	8,481.66	8,462.16

Average: $\Delta E_c/M = 8,469.9 \text{ cal/g}$
 Std. Dev. = $\pm 3 \text{ cal/g}$

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Table V

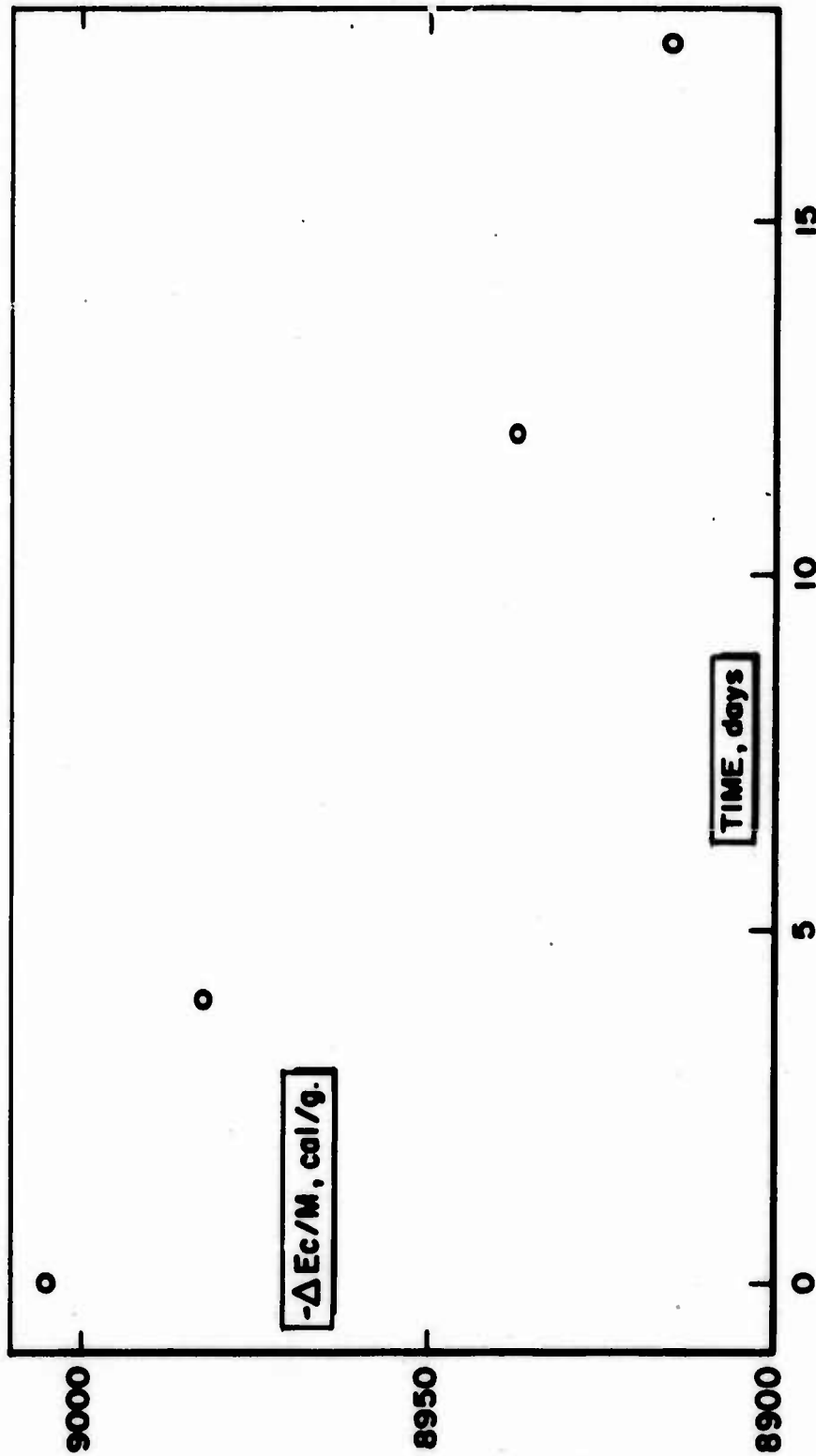
Heat of Combustion Experiments for ELF-101

Parameter	Experiment Number			
	1	2	3	4
ELF-101, g	0.526429	0.623251	0.481497	0.464134
Paraffin oil, g	0.213894	0.173300	0.245916	0.266040
Fuse, g	0.003003	0.002439	0.003155	0.003253
Mole of $\text{HNO}_3 (\times 10^3)$ final	0.703	0.738	0.730	0.730
Mass of glass, g	0.1300	0.1398	0.0944	0.05940
Mass of Pt added, g	51.0279	51.0279	51.0279	51.0279
t_i , °C	22.76638	22.83500	22.87885	22.94780
t_f , °C	24.92091	25.09520	24.99467	25.08134
Δt_{corr} , °C	0.07200	0.05774	0.05815	0.05940
$-\Delta E_c/M$, cal/g	-9,005.23	-8,981.75	-8,936.95	-8,915.42

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(c) Fig. 2 - Variation of Heat of Combustion of ELF-101 with Time

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(C) Results for ELF-101 show a trend with time as illustrated in Figure 2. Apparently some process such as isomerization, polymerization, or decomposition is taking place, which results in a steadily decreasing heat of combustion. It is planned to obtain data on freshly distilled samples to further check this behavior and possibly obtain a reasonably correct value.

(U) The results from paraffin oil were used in the calculations for the ELF compounds, but are also of interest in themselves, since half the experiments were run with the neat paraffin oil and half with the oil enclosed in Mylar film. The two series are in excellent agreement and give added confidence to work previously reported done by the Mylar film technique.

C. HEAT OF COMBUSTION OF ANILINE HYDROCHLORIDE (U)

1. Introduction (U)

(U) Perchlorates are important compounds in propellant chemistry. Thermochemical data have been obtained on such compounds as nitronium perchlorate, hydrazine diperchlorate, and INFO-635 by various means. Many inorganic perchlorates and all organic perchlorates can be thermochemically investigated by the heat of combustion technique. Baroody and coworkers (2) have published an outline for the calculation of heats of formation of compounds containing C, H, Cl, N, and O from raw heat of combustion data. The heat of combustion of aniline hydrochloride was determined to test this outline as well as our laboratory techniques. The heat of formation of aniline hydrochloride can be determined by a heat of solution approach as a check on the combustion result.

2. Material (U)

(U) Aniline hydrochloride was prepared by dissolving about 29 g in 365 ml of dry ether and bubbling in dry hydrogen chloride until it was no longer absorbed. About 34 g (85% of theory) of white product was separated by filtration and washed with 300 cc of dry ether. The product was dried by heating overnight in a vacuum oven at 50°C. The dried material melted sharply at 198°C (literature m.p. 198°C) and analyzed 27.3% chlorine (theory 27.3%). The purity by reaction with bromine was 99.8%.

(U) A sample of Dow aniline with a purity of 99.9 mole % by freezing curve analysis was used for heat of solution work.

3. Equipment (U)

(U) A typical rotating bomb calorimeter and a platinum lined combustion bomb were employed for the heat of combustion studies. For heat of solution work the same type of equipment was used, except that a glass ampoule attached to a breaking mechanism was substituted for the bomb in the calorimeter.

4. Procedure (U)

(U) Samples were pelleted and placed in a platinum crucible which was then suspended in a gimbal attached to the bomb lid. Approximately 20 g of 0.08 M As_2O_3 solution was accurately metered to the bomb by means of a weight buret. The bomb was closed and charged with purified oxygen to 30 atm pressure. After equilibrium in the calorimeter, the charge was electrically fired and the resulting heat release measured by means of an automatic resistance bridge. After the calorimetry the bomb was carefully discharged, opened, and the solution recovered for analysis for nitrate and unoxidized arsenious oxide.

(U) For heat of solution studies, aniline hydrochloride or liquid aniline was sealed in a thin walled glass ampoule and the calorimeter canister was filled with water containing a slight excess of NaOH (for aniline hydrochloride) or a corresponding mixture of NaCl and NaOH (for aniline). At the appropriate moment, the ampoule was broken and the solution process took place.

5. Calculations (U)

(U) The outline published by Baroody et al. (2) was programmed for computer calculation. Some of the necessary parameters were estimated, while others were taken from recent publications. A list of these parameters is given in Table VI. Constant factors for the computer program are given in Table VII.

Table VI

Parameters for Washburn Corrections
for C-H-Cl-N-O Compounds

Item	Symbol	Value	Reference
29h	g^1	0.9973	Estimated
51	$K(\text{CO}_2)$	0.033	(3)
66	g^f	[0.996-.0137 at % (HCl)]	Estimated
69	$\left(\frac{\partial E}{\partial P}\right)_t^1(\text{soln})$	-.00186 cal/g atom	Estimated
69a	$\left(\frac{\partial E}{\partial P}\right)_t^f(\text{soln})$	-.00170 cal/g atom	Estimated
71b	$\Delta E(\text{CO}_2)\text{soln}$	-4000 cal/mole	Estimated, cf. (3)
91a	$\Delta E(\text{As}_2\text{O}_5)\text{decomp}$	76500 cal/mole	(4)

Table VIIConstant Factors for Calculations of Heat
of Combustion of Aniline Hydrochloride

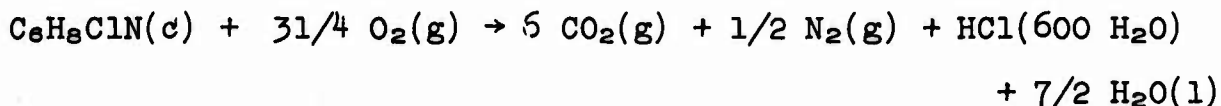
Formula of compound	C ₆ H ₅ ClN
Formula of fuse	CH _{1.8} O _{0.9}
Density of compound	1.222
Density of fuse	1.5
Bomb volume	0.349 liter
Initial oxygen pressure at 25°C	30.3 atm
Reference temperature	25°C
Final ratio H ₂ O/HF	600
($\partial E/\partial P$) _t of compound	-0.003 cal/g/atm
ΔE_c° of fuse	-111.7 kcal/mole
C _p of compound	0.29 cal/g/°C
C _p of fuse	0.4 cal/g/°C
E(calor)	3427.20 cal/°C

6. Results (U)

(U) The heat of combustion results are tabulated in Table VIII. The average value and a molecular weight of 129.590⁴ yield:

$$\Delta E_c^\circ = -799.52 \pm 0.29 \text{ kcal/mole}$$

corresponding to the reaction:



Correcting to constant pressure conditions:

$$\Delta H_c^\circ = -800.26 \pm .29 \text{ kcal/mole}$$

Table VIII
Heat of Combustion of Aniline Hydrochloride

Parameter	Experiment Number					
	1	2	3	4	5	6
Sample wt., g	1.08917	1.08383	1.09075	1.09204	1.09822	1.10036
Fuse, g	0.00415	0.00375	0.00278	0.00341	0.00310	0.00312
N ⁱ (H ₂ O)	1.1558	1.1553	1.1668	1.1561	1.1548	1.1558
N ⁱ (As ₂ O ₃)	0.002104	0.002108	0.002126	0.002134	0.002133	0.002124
N ^f (HNO ₃)	0.000564	0.000661	0.000645	0.000613	0.000693	0.000774
N ^f (H ₂ PtCl ₆)	0.00017	0.000011	0.000012	0.000018	0.000009	0.000010
N ^f (As ₂ O ₃)	0.001344	0.001334	0.001323	0.001339	0.001352	0.001285
ΔE _{ign} , cal	0.47	0.41	0.40	0.39	0.41	0.38
t _i , °C	22.96672	22.96672	22.96678	22.96671	22.96668	22.96675
t _f , °C	25.01183	25.00306	25.01360	25.02069	25.03117	25.03836
Δt _{corr} , °C	0.06976	0.06968	0.06913	0.07452	0.07368	0.07431
-ΔE _c /M (cal/g)	6169.63	6172.03	6169.66	6166.04	6168.38	6171.64

Average: -ΔE_c/M = 6169.56 cal/g

Std. dev. = 1.11 cal/g

With auxiliary data from Wagman et al. (5),

$$\Delta H_{f298}^{\circ} = 42.97 \pm 0.29 \text{ kcal/mole}$$

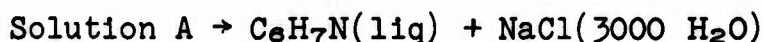
(The uncertainty is taken as twice the standard deviation.)

(U) Results of the heat of solution work are given in Table IX. Electrical calibration of the system gave $E(\text{calor})$ as $3667 \pm 3 \text{ cal/}^{\circ}\text{C}$. From the data there is derived:

(1) $\Delta H = -3.37 \text{ kcal/mole}$ for the reaction:



(11) $\Delta H = -0.58 \text{ kcal/mole}$ for the reaction:



(111) $\Delta H = -3.95 \text{ kcal/mole}$ for the reaction:



With auxiliary data for NaOH, NaCl, and H₂O from Wagman et al. (5) and the heat of formation of liquid aniline, $+7.47 \pm 0.20 \text{ kcal/mole}$, from Hatton et al. (6), there is derived for aniline hydrochloride:

$$\Delta H_{f298}^{\circ} = -42.0 \pm 0.3 \text{ kcal/mole}$$

Table IX

Heat of Solution of Aniline and
Aniline Hydrochloride in Aqueous NaOH

<u>Expt.</u> <u>No.</u>	<u>Sample Mass,</u> <u>grams</u>	<u>Corrected Temp.</u> <u>Rise, $^{\circ}\text{C}$.</u>	<u>Heat of Solution,</u> <u>cal/g</u>
1 ^a	6.9311	0.04910	-25.98
2 ^a	6.9227	0.04919	-26.06
3 ^b	5.007	-0.00614	+ 4.50

^aAniline hydrochloride.

^bAniline.

(U) The difference between the combustion and solution results is slightly larger than the combined statistical errors, pointing to a small systematic error in one or both approaches. The difference is not serious, however, and it appears that the heat of formation of C-H-Cl-N-O compounds, such as organic perchlorates, can be determined with satisfactory accuracy by the heat of combustion method.

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Security Classification

DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1 ORIGINATING ACTIVITY (Corporate author)		2a REPORT SECURITY CLASSIFICATION
The Dow Chemical Company Midland, Michigan 48640		Confidential
		2b GROUP
		Group IV
3 REPORT TITLE		
Investigation of the Thermodynamic Properties of Propellant Ingredients		
4 DESCRIPTIVE NOTES (Type of report and inclusive dates)		
Quarterly Progress Report (1 April to 30 June 1968)		
5 AUTHOR(S) (Last name, first name, initial)		
Sinke, G.C. and Stull, D.R.		
6 REPORT DATE	7a TOTAL NO OF PAGES	7b NO OF REFS
July 1968	29	6
8a CONTRACT OR GRANT NO	9a ORIGINATOR'S REPORT NUMBER(S)	
FO4611-67-C-0025		
8b PROJECT NO	9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
3145	AFRPL-TR-68-144	
8c BPSN-623148		
8d Program Structure 750 G		
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11 SUPPLEMENTARY NOTES		12 SPONSORING MILITARY ACTIVITY
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13 ABSTRACT (C) Heat of combustion measurements on perfluoroammonium fluoborate from Shell Development Company gave erratic results. The amount of sample available is limited and not sufficient to allow tracing down the reasons for the failure of this technique. A differential scanning calorimeter requiring only a few milligrams of sample was successfully used to measure the heat of decomposition and this approach yielded a preliminary heat of formation of -319 ± 10 kcal/mole. Further work on the heat of decomposition is planned to improve the accuracy and to better establish the products of decomposition.		
(C) The heat of formation of a sample of aminoethylaziridine (Code ELF-100), $C_4H_{10}N_2$, from Esso Research and Engineering Company was derived as 212.69 kcal/mole from heat of combustion measurements. Work on methyldiazabicyclo-octane (Code ELF-101), $C_7H_{14}N_2$, also from Esso, revealed the heat of combustion to be decreasing with time, indicating some slow chemical change taking place. No accurate heat of formation could be obtained.		
(U) The heat of combustion of aniline hydrochloride (synthesized at Dow) was measured and a new computerized data reduction program used to derive a heat of formation of -43.0 kcal/mole. This is in reasonable agreement with -42.0 kcal/mole from heat of solution data and it is concluded that no serious systematic errors remain in the data reduction program.		

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Heat of Combustion						
Heat of Formation						
Heat of Solution						
Aniline Hydrochloride						
Perfluoro Compound						
Aza Compounds						

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